INVESTIGATION OF THE LASER FLASH ANALYSIS METHOD TO MEASURE THE THERMAL DIFFUSIVITY OF NANOSCALE IONIC MATERIALS

A Thesis

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In Partial Fulfillment of the Requirements for the Degree of

Master of Science

by

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ABSTRACT

Nanoscale ionic materials (NIMS) are a hybrid organic-inorganic liquid-like material consisting of a hard inorganic nanocore and an organic canopy. The high nanoparticle content, zero vapor pressure and inexpensive mass production capabilities give NIMS the ability to develop into sustainable metamaterials that outperform traditional nanofluids in cost and efficiency. Current heat transfer materials are limited by nanoparticle saturation. NIMS, with their superior nanoparticle concentration and stability, may be a more effective and environmentally friendly substitution for these products. Investigation of this requires a reliable method of determining the thermal diffusivity of NIMS. The laser flash analysis (LFA) method of experimentally determining the thermal properties of nanofluids was applied to NIMS of varying compositions at room temperature. Despite promising preliminary results, LFA is not yet a reliable method of characterizing the thermal properties of NIMS. In spite of obstacles in experimental measurement, LFA still appears to be the most viable method for thermal measurement of NIMS. Further improvements to experimental techniques may lead to standardization of thermal diffusivity of NIMS.

BIOGRAPHICAL SKETCH

Michelle Wu was born on September 29, 1986 in Columbia, Maryland to Drs. En and Angela Wu. She attended Smith College in Northampton, Massachusetts from 2003 to 2007 during which time where she completed internships focused on optical techniques and quantum sciences including a summer at Jet Propulsion Laboratory in Pasadena, California. Upon graduating with a Bachelor of Arts in Physics, Michelle moved to Ithaca, New York and joined the Giannelis group at Cornell University. She was awarded the National Science Foundation Graduate Research Fellowship in 2008, and has spent her tenure as a NSF fellow learning from and working with many talented and inspirational scientists.

For Mama, Dad, Michael, and Kalina

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Finally to my family and all the friends I have made in Ithaca. Thank you.

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I. Nanoscale Ionic Materials

Nanoscale ionic materials (NIMS) are a new materials platform recently discovered at Cornell University. NIMS are organic-inorganic hybrids consisting of three parts: a nanoparticle core, a charged corona, and a canopy. NIMS are unique in terms of nanomaterials because of their tunability, solventless nature, and high stability. Due to their hybrid architecture, their components may be chosen to display specific characteristics. At room temperature, NIMS may appear and flow as simple liquids but unlike in ordinary fluids, the particles carry themselves in their own suspending medium, and therefore NIMS have zero vapor pressure. The ionic attraction between the corona and canopy provides added stability.

NIMS have the potential to be useful in many practical applications and may replace many traditional materials. Potential applications of NIMS include heat transfer materials, inks, lubricants, environmental cleanup, and energy production. The NIMS structure addressed in this thesis are second generation NIMS with an architecture containing a silica core and amine canopy.

Synthesis of NIMS

The overall structure of NIMS synthesis involves three components: (1) A core of colloidal silica, (2) corona of sulfonic acid groups, (3) an amine canopy. The two cores studied were Ludox HS30 and Ludox TM40 (Sigma Aldrich). HS30 is a 30% solution of 12 nm SiO_2, TM40 is a 40% solution of 22 nm SiO_2.

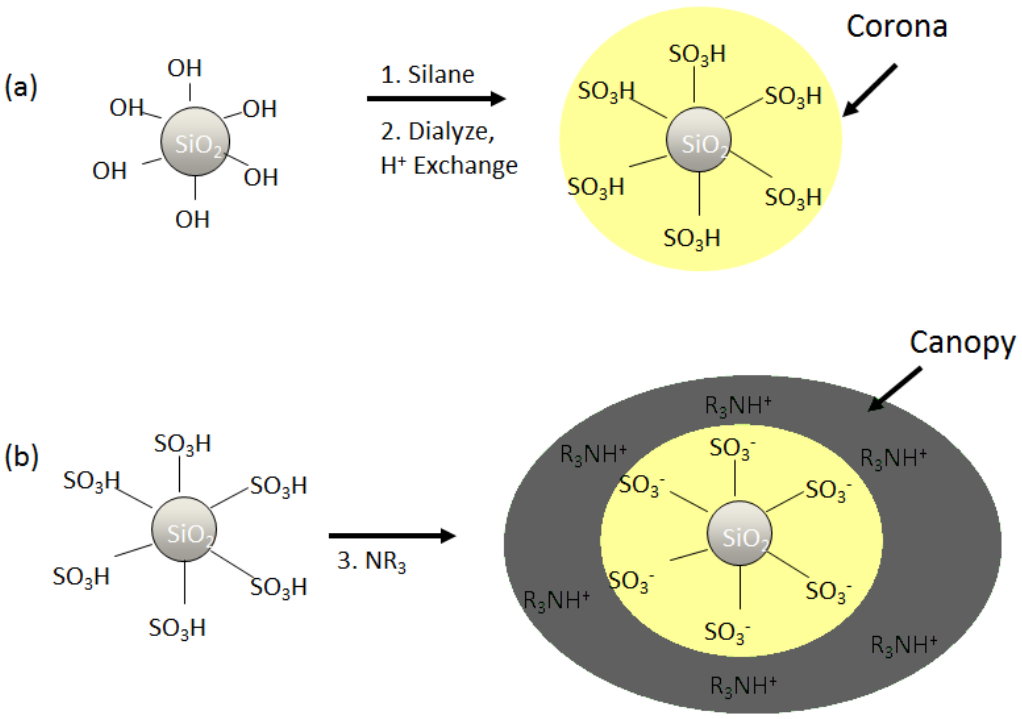

Figure 1: Schematic showing the various steps in NIMS synthesis

Colloidal silica was diluted to a concentration of 3.75 wt/wt% in 18.2 MΩ-cm deionized (DI) water and sonicated. 3-(trihydroxylsilyl)-1-propane sulfonic acid (SIT, Gelest) was diluted to a concentration of 8 wt/wt% in DI water and vigorously stirred. The silica solution was added dropwise into the SIT solution and also mixed well. A 13 wt/wt% mixture of sodium hydroxide (NaOH, 1M, Sigma Aldrich) was added dropwise and monitored by a Fisher Scientific Accument Excel XL25 pH/mV/Temperature/ISE meter until the solution reached a pH of 5. This solution was placed in a sealed flask and stirred at 70 °C for 24 hours then cooled to room temperature.

Next, the core-canopy solution underwent a dialysis treatment over four days to remove unreacted SIT and salts. The solution was placed in Snakeskin 10K MWCO

dialysis membranes (Thermo Scientific) and suspended in deionized water. The water was changed four times to ensure a concentration gradient across the membrane. The solution was run through columns filled with HCR-W2 ion exchange resin (Dowex) to remove the Na^+ and protonate the sulfonic acid groups as show in Figure 2. The concentration of this functionalized silica solution was used to determine the amount of primary amine needed to obtain the desired silica weight percentage. This equivalence point occurs at a ratio of 1:1 nanoparticle cores to counter ions.[1] A solution of primary amine molecules (Huntsman, Jeffamine-$NH_2(CH_2CH_2O)_nCH_3$) in DI water was added dropwise to the acidic functionalized silica. The three amines used were XTJ-505 and XTJ-506, and M2070, with molecular weights of 600 MW, 1000 MW, and 2000 MW, respectively. The amine reacted with the sulfonic acid in an acid-base reaction that created an ionic attraction between the corona and canopy. The final solution was left in a vacuum oven at 33 °C and dried, removing all water.

Due to the three-component system of NIMS, the properties can be easily tuned. For example, to increase viscosity, a lower concentration or molecular weight of amines may be used. To produce a hard, solid sample, increased core concentrations may be used.[2]

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II. Heat Transfer Fluids

Heat transfer fluids have extensive applications that include uses in electronic cooling, energy production (solar and nuclear power plants), refrigeration, transportation, and microelectronics.[1-5] Most common and traditional liquids used as heat transfer fluids, such as water and ethylene glycol, have low thermal conductivities and face limitations such as finite physical space available for a heat management system.[5]

Material	Thermal Diffusivity, 22 °C
Water	1.43×10^{-3} cm^2/s
Ethylene Glycol	9.41×10^{-4} cm^2/s
Brine (50% salinity)	1.48×10^{-3} cm^2/s

Chart 1: Thermal diffusivity values for traditional heat transfer fluids

Advances in heat transfer fluids have indicated that suspensions of solids in fluids highly enhance thermal conductivity, which increases the performance of a heat transfer fluid. In fact, enhancement of the thermal conductivity of a conventional fluid with the addition of millimeter or micrometer sized particles has been used for over 100 years but is limited by sedimentation, erosion, and inhomogeneity.[6] These fluids also face space limitations and propensity for oversaturation.

Heat transfer takes place at the surface of the particle, and therefore it is ideal to use particles with a large total surface area. The surface-area-to-volume ratio is

1000 times larger for particles with a 10 nm diameter than for particles with a 10 um diameter, making it desirable to suspend even smaller particles in fluid.[7]

Nanofluids

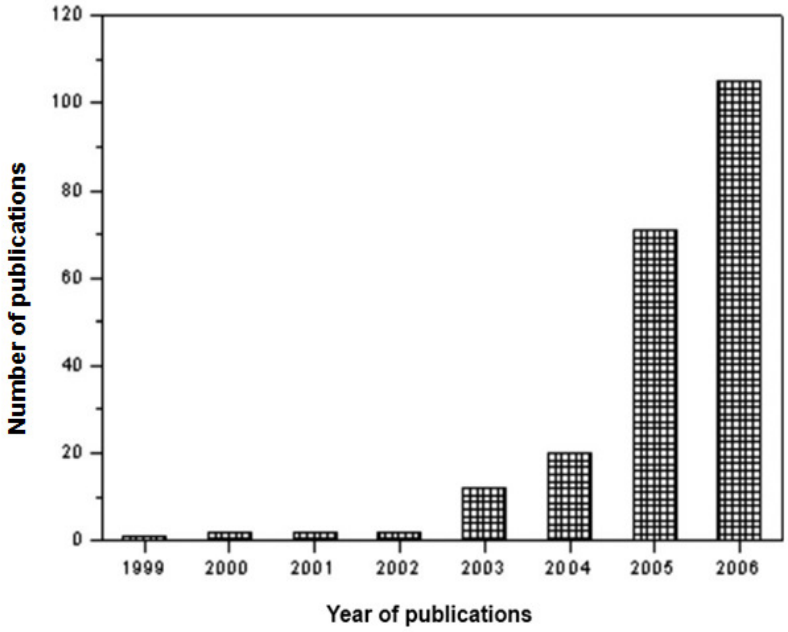

Figure 2: Compiled data showing increase in publications about nanofluids from the Science Citation Index[11]

A nanofluid is a suspension of nanometer sized particles in a base liquid. Nanofluids have been the subject of intense studies, with a dramatic rise in research on nanofluids in science and technology in the past decade.[11] Many of these investigations focus on nanofluids as thermal conductivity enhancers. [4-8, 14] Nanofluids are superior to traditional materials in that they exhibit behavior more similar to a single-phase liquid than a solid-liquid mixture; moreover, they are more stable and have higher heat transfer coefficients. The exact mechanisms behind the increased thermal conductivity of nanofluids are still unclear and often disagreed upon by

researchers[4-6]; there have been extensive studies to determine a correlation between the presence of nanoparticles with increases in thermal conductivity in terms of Brownian motion, particle concentration, cluster formation, particle shape, and many more variables.[9] Currently, the only consensus among researchers is that there are clear relationships between thermal conductivity and nanoparticle size, volume fraction, and uniformity of dispersion, with nanofluids showing extreme potential in improving heat transfer materials.[3,4,8-10] Prior research supports that: smaller nanoparticles yield higher thermal conductivities due to a larger surface-to-volume ratio, higher concentration and volume fraction of nanoparticles increase thermal conductivity, as seen in Figure 4; the more evenly dispersed the particles, the greater the thermal conductivity (Figure 5).

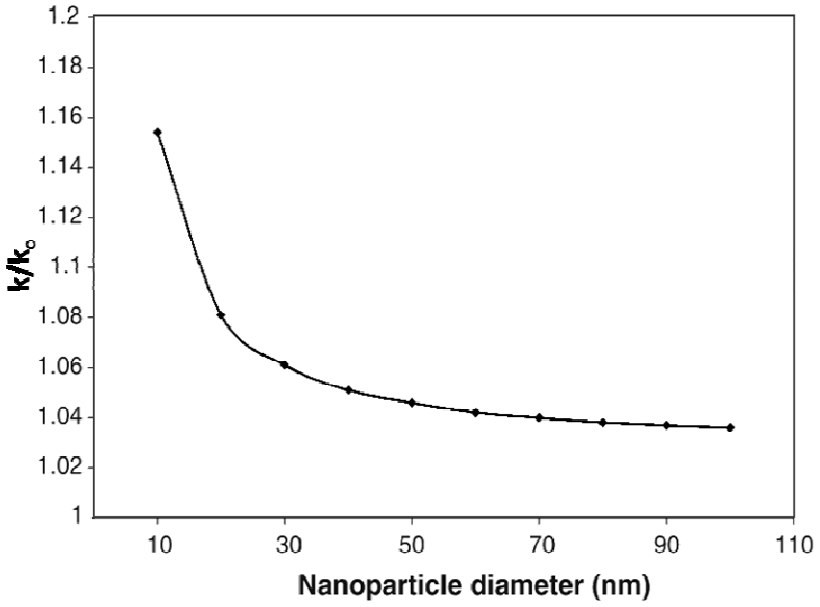

Figure 3: Theoretical thermal conductivities of alumina nanoparticles suspended in water as a function of particle size, k/k_o= nanofluid conductivity/base fluid conductivity[8]

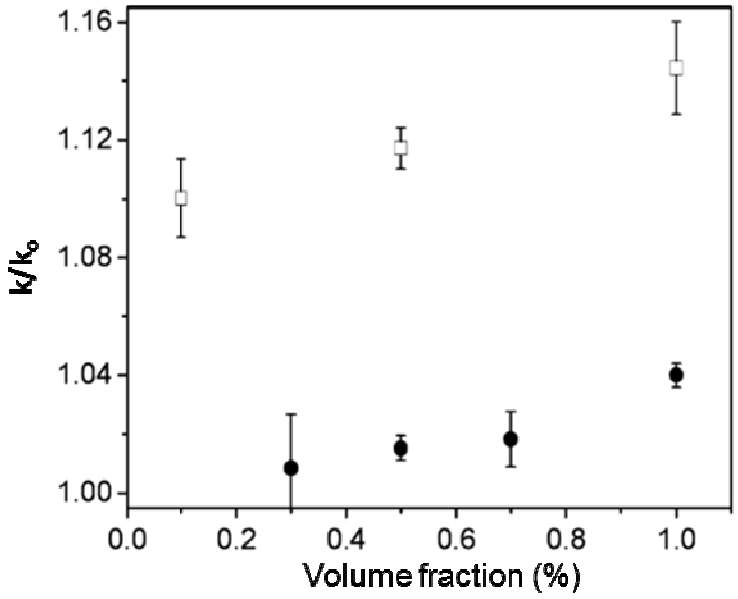

Figure 4: Thermal conductivies of TiO_2 (squares) and Al_2O_3 (circles) nanofluids as a function of volume fraction in deionized water.[10] k and k_o are the thermal conductivities of the base fluid and nanoparticle respectively.

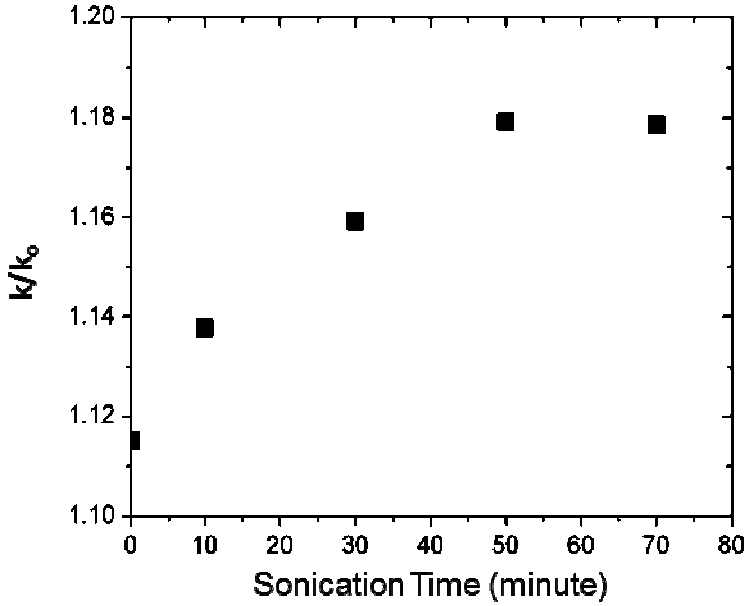

Figure 5: Thermal conductivity of Fe nanofluids as a function of sonication time.[3] Thermal conductivity increased as sonication time increased. k and k_o are the thermal conductivities of the nanofluid and ethylene glycol, respectively

Nanofluids vs. NIMS

Nanofluids show promise as heat transfer materials but still face many limiting issues such as stability, presence of hazardous solvents, and the high cost of nanoparticles. There has been much controversy surrounding the use of nanofluids for effective thermal applications like cooling, with one of the most cited reasons being the stability and safety of nanofluids: if the suspending medium evaporates, the suspension is destroyed with potentially harmful nanoparticles remaining and possibly aerolizing, leading to health and environmental hazards. The particle concentration required to significantly improve thermal conductivity has also been called into question. A nanofluid is still a mixture of particle and base fluid, and therefore suffers from a dispersion limit. With finite particle dispersability comes phase separation that is detrimental to the performance of the nanofluid unless the nanofluid is in constant motion. In this case the costs highly outweigh the benefits.[12]

With the general disagreement surrounding nanofluids and challenges nanofluids face, the use of NIMS may be a practical alternative to nanofluids as heat transfer materials. With single-phase nature, high-nanoparticle content, and homogeneity, NIMS can be expected to significantly outperform ordinary nanofluids in heat transfer applications. In addition, NIMS can replace toxic materials. By manipulating the nanoparticle chemistry and structure, NIMS exhibiting a broad range of physical and chemical properties can be synthesized to meet special heat transfer requirements, not just fluid needs, but solid insulations and gel packing materials. NIMS synthesis is also highly scalable, leading a much more cost-effective production.

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III. Thermal Diffusivity

Thermal diffusivity is the rate at which heat flows through a material and is related to a material's thermal conductivity in

(Eq. 1) $$\alpha = \frac{\kappa}{\rho C_p}$$

Where κ is the thermal conductivity (W/(m·K)), ρ is the density (kg/m^2), and C_p is the specific heat capacity. ρC_p is also referred to as the volumetric heat capacity. Depending on the purpose of a heat transfer material, a high or low diffusivity is ideal. For example, a low thermal diffusivity indicates a low thermal conductivity which results in a high thermal resistance (R), leading to an excellent insulator, minimizing heat loss (R~ 1/k ~ 1/α)

Methods of Measurement

The methods of determining the thermal diffusivity and conductivity of materials are divided into two classes: steady state and transient. Steady state measurements employ a non-changing unidirectional temperature gradient and are highly reliable for solids. They are unreliable and inconsistent for anything ranging in viscosity from gel-like to liquid. Other downfalls are the high volume needed for accurate measurement and longer measurement times required to account for convective disturbances.[1,2] In considering characterization methods for NIMS, only transient methods were considered.

Transient Hot Wire Method

Transient hot wire (THW) method is an established technique that is widely used for thermal conductivity measurements. In THW, a thin wire with length to radius ratio L/r << 200 is suspended in a closed cylindrical container filled with the sample. The wire is usually platinum due to platinum's stable electrical properties and resistance to corrosion. The wire acts as both a heating element as well as thermometer. The temperature over time response of the wire to an electrical pulse is recorded. The wire produces a constant heat flux per length, q, and the change in temperature of the wire is related to the thermal diffusivity by Equation 2:

(Eq. 2) $$\Delta T(t) = \left({}^{q}/_{4\pi\alpha}\right) ln\left({}^{4\kappa t}/_{C r_0^2}\right)$$

Where r_o is the radial distance and C is calculated constant $C = e^{\gamma}$ where γ is Euler's constant. α and κ are the thermal conductivity and diffusivity respectively.[3,4] Further derivations by Eastman yield a simpler relationship:[3,4]

(Eq. 3) $$\alpha = \left({}^{q}/_{4\pi\Delta T}\right) ln\left({}^{t_2}/_{t_1}\right)$$

The measurement time needed in THW is much shorter than that in steady state methods; however, a large volume of material is still required and thus the sample is susceptible to thermal disturbances.[1,7] Despite the success of the transient hot wire method of measuring thermal conductivity, it cannot be reliably applied to electrically conducting and ionic materials due to the electrical current travelling through the wire. Issues that would arise are current flow through the sample, polarization on the surface of the wire, interaction between the metallic casing and wire, all leading to distortion of measurements.[7] There have been many advances made

in THW with the introduction of insulating coatings on the wire or altering the length of the wire, but with those modifications have come much debate over the necessity of insulating a wire and the accuracy of such measurements.[8-10] With these considerations in mind, the laser flash analysis method (LFA) was chosen for thermal characterization of NIMS.

Laser Flash Analysis Method

The flash method was first used in 1961 by Parker et al[11] and the laser flash method of determining thermal diffusivity in 1979 by Takahashi et al.[12] The laser flash method is a transient heat flux method that measures directly thermal diffusivity and indirectly thermal conductivity. Technology and developments since 1979 have improved the accuracy and data fit models that the LFA uses to produce a very reliable method of not only measuring thermal diffusivity, but also heat capacity of materials ranging from solids to liquids.[13-18] Other advantages to using modern LFA technology are experimental convenience, i.e. the ability to place the sample in a furnace or vacuum system and choose the atmosphere.

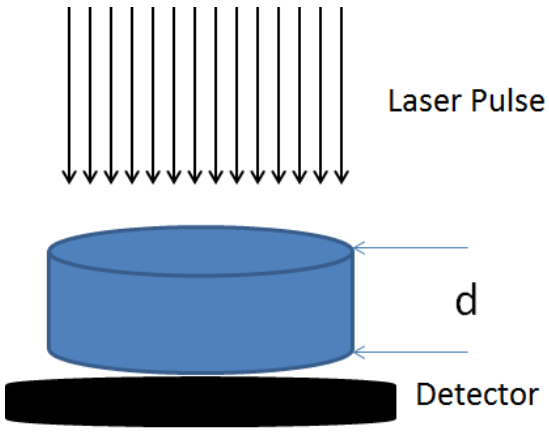

Figure 6: Schematic of laser flash method mechanism with a laser source striking the sample from above. The infrared detector below records the temperature change over time.

LFA employs a laser beam as a heat source. This high energy pulse is aimed at one side of a sample of known thickness *L*, typically less that 1 mm. The energy is absorbed at the initial surface of the sample and the temperature response upon exiting is recorded by high speed infrared sensors as shown in Figure 6. Thermal diffusivity values are computed from the temperature rise versus time data. This is an improvement over the transient hot wire method because it essentially eliminates the effects of convective heat transport during measurement. The instantaneous temperature response requires a substantially shorter measurement time than THW. [18] In addition, this method uses light rather than electrical current as a heat source, allowing for the process to be applied to electrically conducting liquids, making LFA ideal for NIMS.

The analytical solution to the one-dimensional thermal conduction equation under assumed ideal conditions for a laser flash measurement gives:

(Eq. 4) $$\Delta T = \Delta T_m \left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(-n^2\pi^2\alpha t / L^2\right)\right]$$

Where L is the thickness of the sample, ΔT is the temperature rise, ΔT_m is the maximum temperature, and t is the time after pulse heating.[14] Further manipulation of this equation yields a now generally accepted relationship for thermal diffusivity:

(Eq. 5) $$\alpha = {0.1388L^2}/{t_{1/2}}$$

Where $t_{1/2}$ is the time to half maximum temperature rise $\Delta T/\Delta T_m = ½$. The ideal conditions assumed are the laser pulse time is negligibly shorter than travel time through the sample ($t_{pulse} << m_{easurement}$), uniform heating, a homogeneous opaque sample and adiabatic boundary conditions.[15,17] Since ideal conditions are rarely met in experimental situations, many scientists have provided real-life corrections to the LFA model. Applied corrections to the original LFA model include radiation and convection loss by Cowan, Clark, and Taylor, and finite pulse effects by Cape and Lehman. Current LFA equipment apply curve fitting and numerous algorithmic refinements and corrections to experimental factors.[17, 21-22] These models now produce more accurate data with temperature response calculated models that give the best fit values for thermal diffusivity measurements.

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IV. Apparatus and Procedure

Thermal diffusivity measurements were taken using a Linseis XFA 500 Xenon Flash Thermal Constant Analyzer (XFALT) paired with Aprosoft Laserflash software, also from Linseis. The Aprosoft interface controlled the XFALT and recorded all data. The capabilities of the XFALT include accommodating sample thickness from 0.1 mm to 6 mm thickness and temperature ranging from -125 °C to 1600 °C with the use of interchangeable furnaces. A graphite sample holder was used for its high and well-established thermal diffusivity, allowing for more accurate measurements.

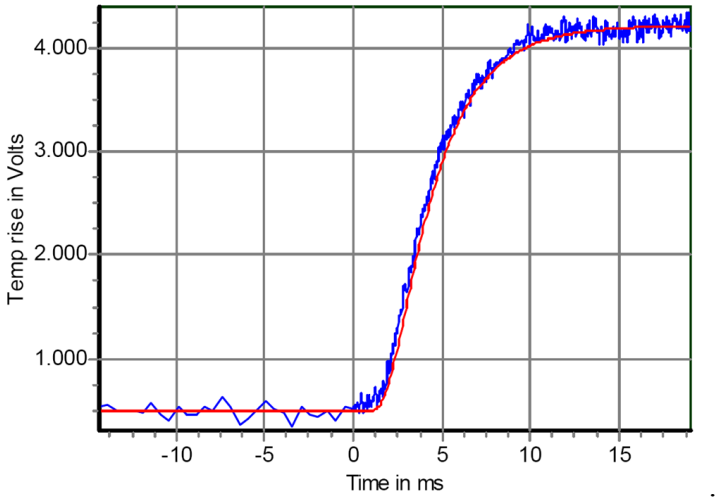

Figure 7: Ideal fit for solid graphite standard with α = 0.2 cm^2/s, 25 °C

The XFALT was calibrated with a solid graphite standard with known thermal diffusivity at 25 °C (Figure 7) and silicon oil with known thermal properties. Samples were loaded into cylindrical 25 mm diameter enclosed graphite sample holders by direct pipetting for less viscous samples or suspension in tetrahydrofuran (THF, Sigma-Aldrich) and evaporation for more gel-like samples. In the instances of the

more viscous samples, 5 mL of THF was added to a vial containing 0.5 g to 1 g of NIMS sample and sonicated for 15 minutes. Part of this solution was then pipetted into the sample holder, which was then placed in a fume hood or vacuum oven.

The height of each sample was recorded and entered into the computer. The sample was then loaded into the XFALT sample robot located in a furnace (Figure 8). The furnace was placed under vacuum and temperature was set to 20 °C. After the heating mechanism reached equilibrium, the detector amplitude was checked. The amplitude must not be more than 0.1. The sample was irradiated with a Xenon flash lamp. The temperature rise at the opposite end of the sample was measured with a high speed IR detector. The temperature change vs. time was graphed and a chosen combined model that integrated heat loss and finite pulse corrections was applied.

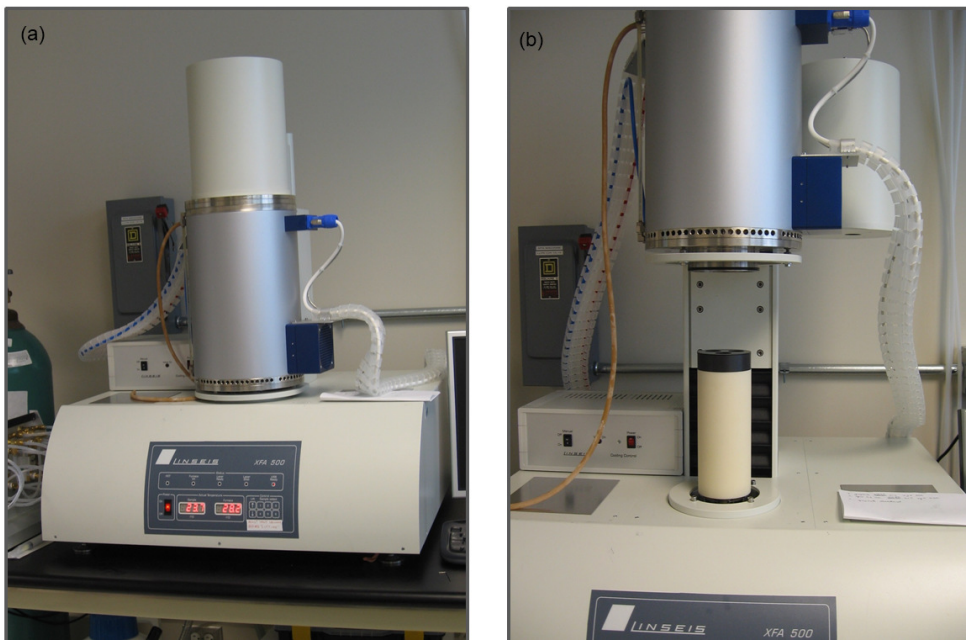

Figure 8: Linseis XFA 500 Xenon Flash Thermal Constant Analyzer, (a) with furnace enclosed (b) three-sample robot, the laser is located in the base of the machine with an IR detector above the furnace

V. Results and Discussion

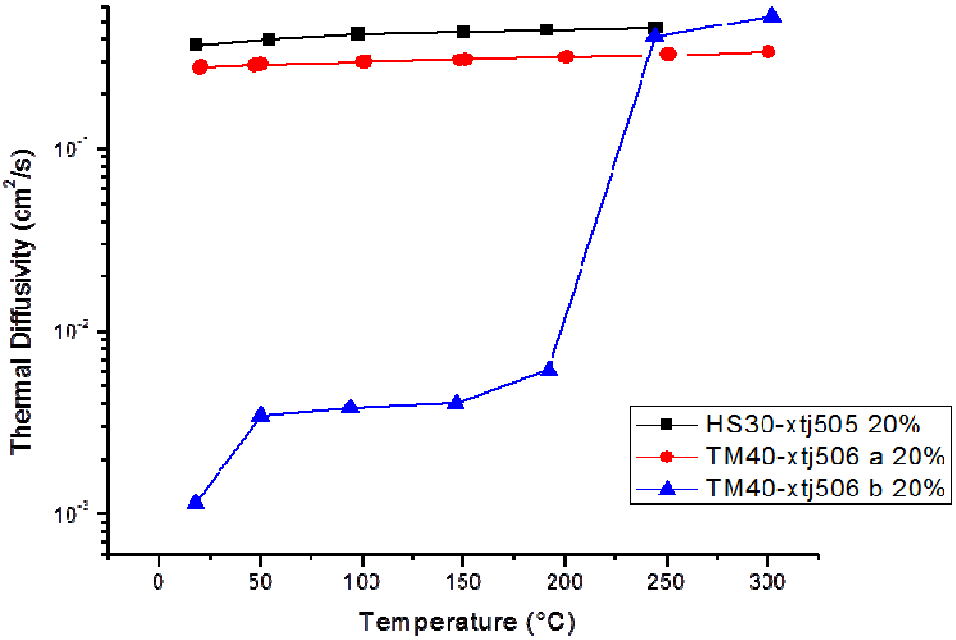

Figure 9: Preliminary thermal diffusivity measurements

Three samples of NIMS with 20% core volume concentration were measured with XFALT on site at the Linseis laboratories for preliminary measurements (Figure 9). These were of interest not only because of the relative high thermal diffusivities at room temperature of HS30-xtj505 and TM40-xtj506a (0.372 cm^2/s, 0.279 cm^2/s), but also because of the abnormal behavior of the second sample of TM40-xtj506. Ignoring first the abnormality, we address the thermal diffusivities of HS30-xtj505 and TM40-xjt506. The smaller nanocore NIMS had a higher thermal diffusivity, which was expected based on studies of nanofluids. In addition, these materials exhibited higher thermal diffusivity than that of SiO_2 ($8.3x10^{-3}cm^2/s$) and on the same order of

magnitude as metals like iron (0.230 cm^2/s). Diffusivity also increased with temperature in all three samples.

These promising results prompted further study of HS30 and TM40 NIMS with primary amine canopies with SiO_2 core volume percentages of 10%, 20%, 25%, and 30% all at 22^oC (Figure 10, Figure 11)

The TM40 core NIMS revealed that lower molecular weight canopies had lower thermal diffusivity at room temperature. The predicted trend was that higher molecular weight canopies would have lower thermal diffusivities. This was also inconsistent with data taken of the HS30 core NIMS, where there was no clear correlation between molecular weight and diffusivity.

The preliminary data and theory based on nanofluid behavior also predicted that the HS30 based NIMS would display larger higher thermal diffusivity than TM40 NIMs. It was expected that smaller particles would have greater diffusivity, but on average they had lower diffusivity. In addition, none of the measurements were on the same order of magnitude of the preliminary results, including the abnormal TM40-xtj506b.

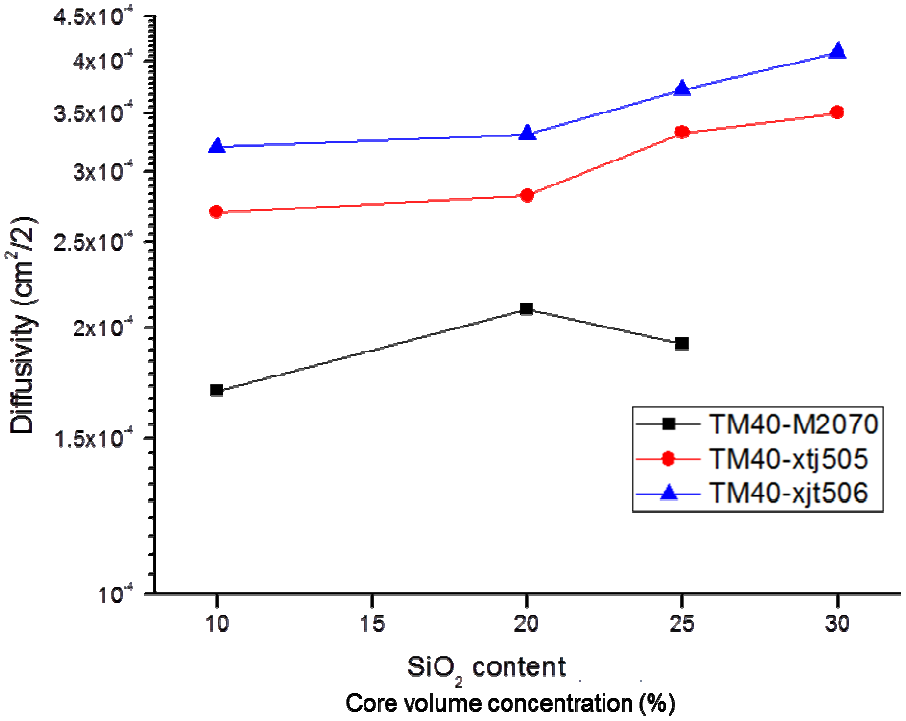

Figure 10: Thermal diffusivity vs. core concentration of TM40 core NIMS

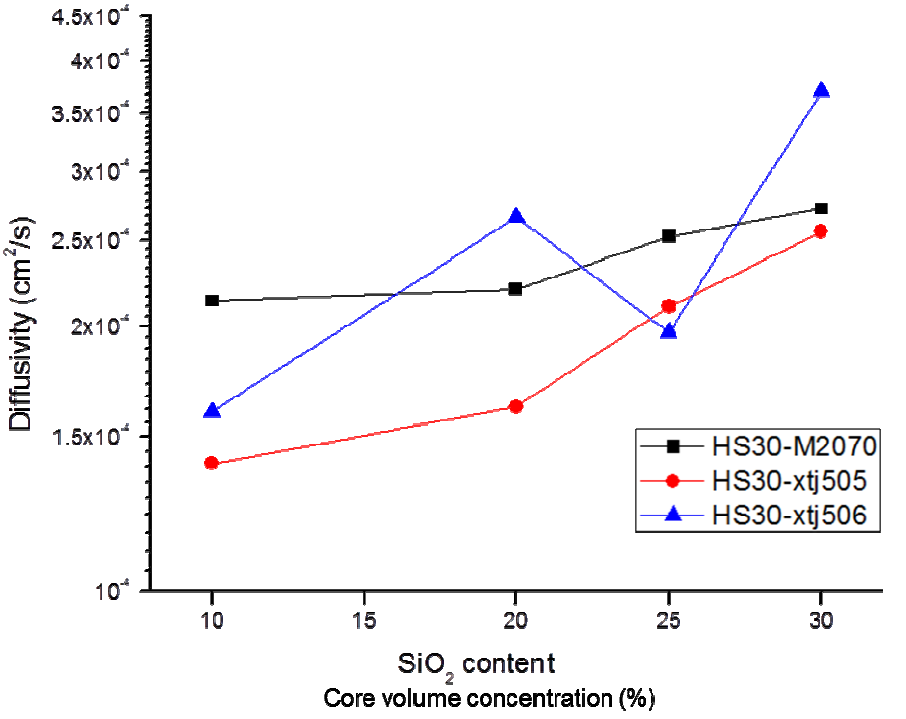

Figure 11: Thermal diffusivity vs. core concentration of HS30 core NIMS

It is evident that there is neither a clear nor consistent correlation between the architecture of NIMS and thermal diffusivity. The thermal diffusivity measured in Germany of HS30-xjt506 at 20 °C was 0.372 cm^2/s, which is three orders of magnitude greater than the experimental value taken on site at Cornell ($\alpha = 1.62x10^{-4}$ cm^2/s). What is of interest is the diffusivity of TM40-xtj506b which showed a large increased in thermal diffusivity at higher temperatures. Since there are no standards to compare the data to, it is unclear which set of results are more accurate.

Challenges

The data presented is only a small portion of the actual measurements taken. Eighty percent of the measurements were not viable. The majority of the measurements produced incomprehensible readings similar to those shown in Figure 12. There is no physical meaning behind the graphs. As stated before, the Linseis machine and software record the temperature change from the initial surface to the back of the sample and apply established algorithms for a best fit. There were many factors that contributed to inconsistent measurements. First, there was much interference in the form of drifting temperatures. The furnace temperature, though preset, fluctuated up to 7 degrees in either direction without provocation. Next, there was much sensor noise present in the sampling. Upon further examination and consultation with Linseis, it was determined that the detector was not sensitive enough. The original sensor was swapped out for a different model, but still produced very sporadic readings. Finally, the XFALT was prone to taking partial

measurements—the laser fired and struck the sample, but no temperature change was recorded.

Other experimental challenges that arose were difficulties in loading NIMS into the sample holders. Though the amount of sample needed was less than 0.4 mL, it was frequently difficult to place a uniform sample in the sample holders. Dispersing the NIMS in a solvent like THF and evaporating the solvent helped improve sample loading. This procedure not only increased sample preparation time by days rather than hours but also often backfired, with a film or bubbles appearing at the surface of the sample.

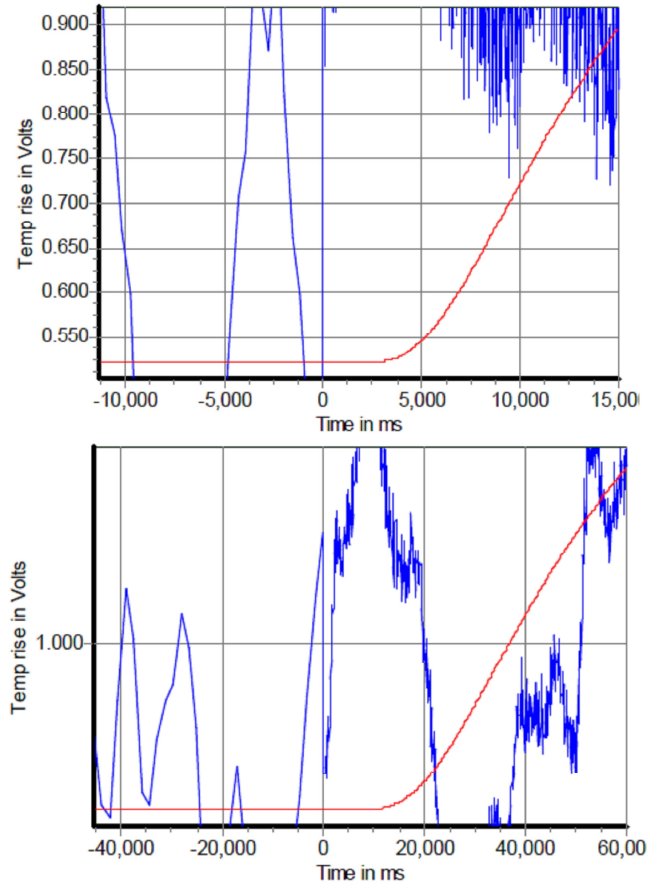

Figure 12: Unusable measurements of 20% TM40-xjt505 at 22 °C

The useable data points adhered to the general model and corrections for temperature rise over time lay out by Cowan, Dusza, Azumi, and Clark and were consistent with standard deviations of less than 7%. These data points are however questionable because of all the discrepancies and obstacles listed above.

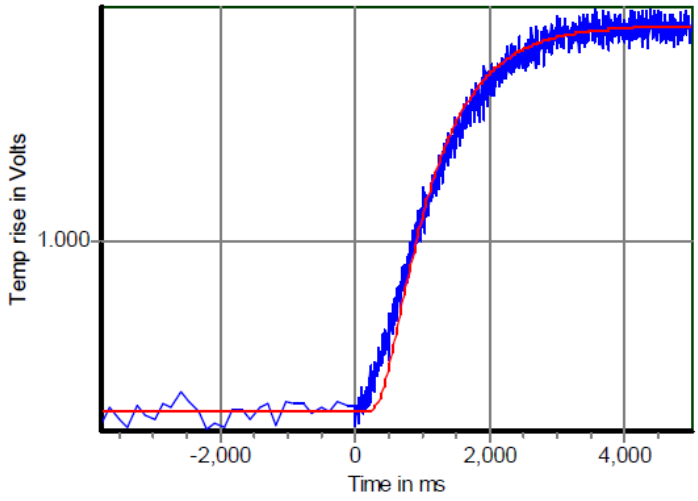

Figure 13: Acceptable fit of temperature rise vs. pulse time

VI. Conclusion

Heat transfer fluids have great importance in many scientific and industrial processes. However, there were few significant improvements in new materials until the development of nanofluids. Existing research indicates that the addition of nanoparticles to a fluid increases its thermal conductivity. This increase depends on the amount of solid nanoparticles in the fluid as the nanoparticles themselves carry heat. Raising the heat conductivity of most nanofluids is challenging because of their finite particle dispersability due to their two-phase nature. One way around this is the use of nanoscale ionic materials (NIMS) developed at Cornell University. In order to explore NIMS as heat transfer materials, their thermal properties, especially thermal diffusivity must be studied.

The most promising method of measuring the thermal diffusivity of NIMS is the laser flash analysis method. The current technology shows promise in eventually becoming a reliable characterization tool, but has not proven dependable for the applications of NIMS. Further improvements in the XFALT machine and software as well as experimental techniques may eventually lead to a standard method of thermal diffusivity measurements of NIMS. The question of whether LFA is applicable to characterizing the thermal properties of NIMS remains unanswered.

Once the characterization methods of thermal properties of NIMS are standardized, future considerations may include investigating the thermal response of NIMS over a large temperature range. NIMS with metal cores have been synthesized, and may also be thermally characterized. If theoretical indications hold true and NIMS behave like nanofluids in terms of thermal enhancements, new materials combining

ideal thermal properties with other physical properties may be produced. Considering the many areas of technology that require heat transfer materials, NIMS may one day play a role in many industries.